

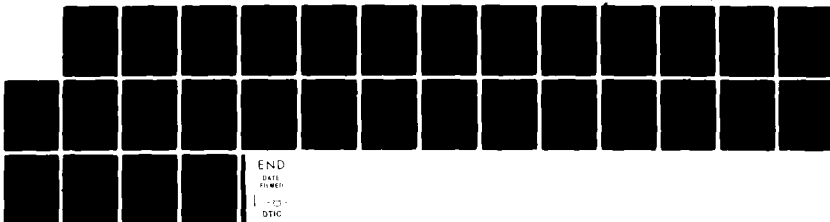
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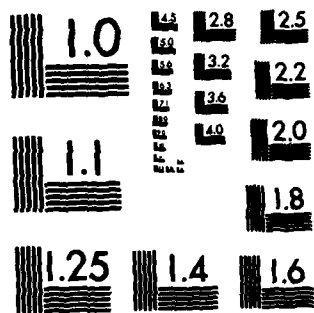
METAL CATALYZED OLIGOMERIZATION REACTIONS OF
ORGANOSILOXANES(U) MICHIGAN UNIV ANN ARBOR DEPT OF
CHEMISTRY M D CURTIS 28 OCT 82 TR-5 N00014-78-C-0191

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by

M. David Curtis

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The University of Michigan
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Ann Arbor, MI 48109

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Metal-Catalyzed Oligomerization Reactions of Organosiloxanes

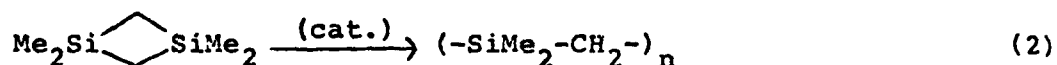
M. David Curtis, Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109

Abstract

Transition metal complexes, e.g. $L_2^{\eta}Pt(C_2H_4^{\eta})$, $L_3^{\eta}RhCl$, and $L_2^{\eta}Ir(CO)Cl$ ($L=Ph_3P$), react with tetraalkyldisiloxanes, $(HRR'Si)_2O$, to produce metallacycles featuring the transition metal, two silicons, and the oxygen in a four-membered ring, $MSiOSi$. When $R=Me$ and $R'=Ph$, stereoselectivity in the formation of the metallacycle from a mixture of stereoisomers of the starting disiloxane is observed. The catalytic activity of these complexes for the oligomerization of the disiloxanes has been investigated in the hope of obtaining stereoregular silicones. It has been found that extensive rearrangements occur which redistribute the groups on the silicon atoms. Increased selectivity for the desired exchange type (SiO-groups for Si-H) was found when the catalysts were adsorbed on oxide supports. Although the goal of synthesizing stereoregular silicones has not yet been achieved, the results warrant further investigation. 

Our research on the metal-catalyzed redistribution reactions of organodisiloxanes had its start several years ago when two lines of research came together. The first of the two lines was our interest in small ring metallacycles which contained in the ring at least one transition element and one or more of the heavier group IVA congeners, e.g. Si or Ge. Small-ring metallacycles are of interest since they have been implicated as intermediates in several transition metal-catalyzed reactions, e.g. olefin metathesis.¹⁻³

Metallacycles are also probable intermediates in several reactions of silacyclobutanes.⁴ For example, several transition metal complexes catalyze the ring-opening polymerization of silacyclobutanes and disilacyclobutanes to high molecular weight polycarbosilanes (eq. 1,2).⁵

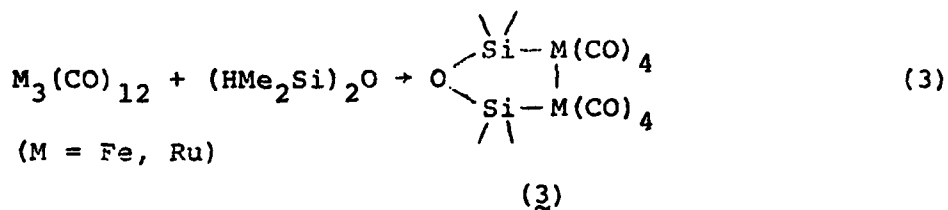


Intermediate, 2, in eq. 1 may also be trapped with acetylenes to form silacyclohexanes.¹⁰

The second line of research which merged into the present work involved the use of polysiloxanes to anchor transition metal complexes for use as "supported homogeneous" catalysts.¹¹ The most-used polymers for supporting transition

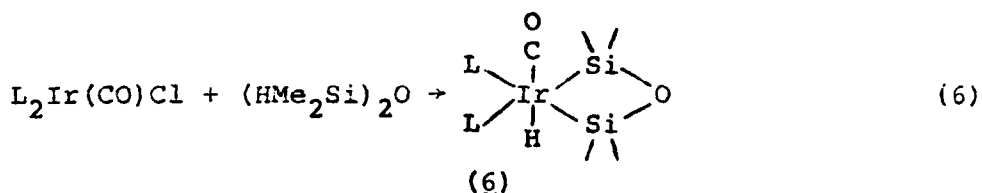
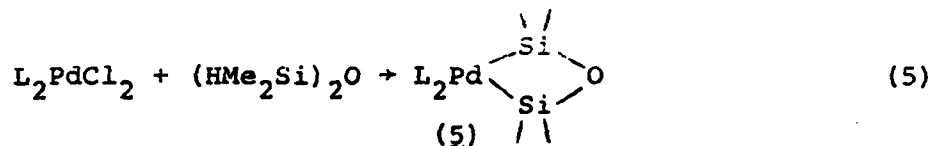
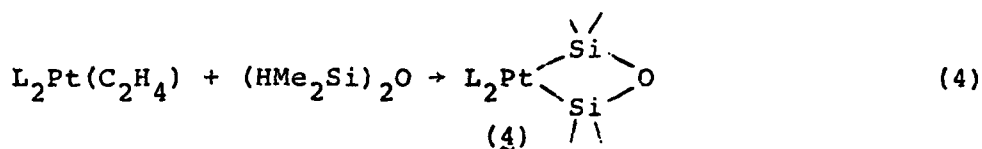
metal complexes are modified, cross-linked polystyrene. Usually, multi-step syntheses are required for the modification and the degree of possible catalyst loading is limited by diffusion problems. We reasoned that transition metal complexes could be attached to polysiloxane polymers of the type, $[-\text{Si}(\text{H})\text{MeO-}]_n$, due to the high reactivity of the Si-H linkage toward low-valent metal complexes.

In fact, the Si-H bonds of the polymer $[\text{Si}(\text{H})\text{MeO}]_n$ react with a variety of low-valent metal carbonyls,¹² but the resulting polymers were unstable, cross-linking and extruding metal complexes upon standing. In order to understand such behavior, we turned to studying the reactions of tetramethyldisiloxane, $(\text{HMe}_2\text{Si})_2\text{O}$, since this disiloxane is the simplest difunctional model characteristics of the repeating unit of the $[-\text{Si}(\text{H})\text{MeO-}]_n$ polymer. It was found that TMDS (tetramethyldisiloxane) reacts ruthenium and iron carbonyls to give the five-membered metallacycles, 3.¹²

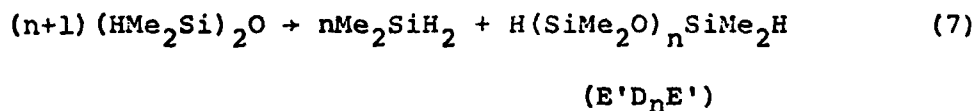


The five-membered metallacycles are relatively inert and possess negligible catalytic activity.

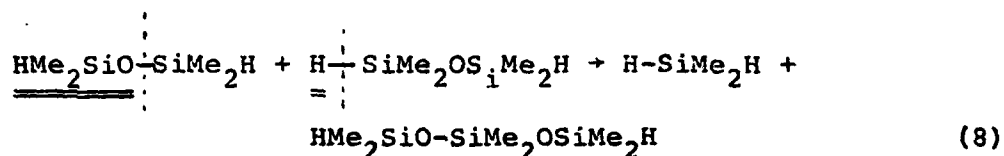
In contrast, complexes of Pd, Pt, and Ir were found to give four-membered metallacycles, e.g. eq. 4-6 ($\text{L}=\text{Ph}_3\text{P}$).¹³



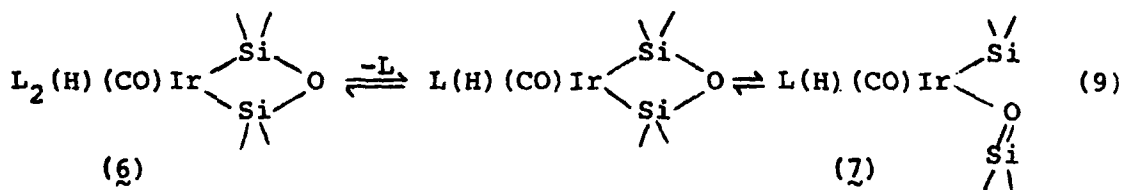
When excess TMDS was used in the synthesis of the metalla-cycles, 4-6, a mixture of siloxane oligomers, $\text{H}(\text{SiMe}_2\text{O})_n\text{SiMe}_2\text{H}$, was observed to form as a byproduct. It was then established that these metallacycles acted as catalysts (or catalyst precursors) for the disproportionation of TMDS as shown in eq. 7.



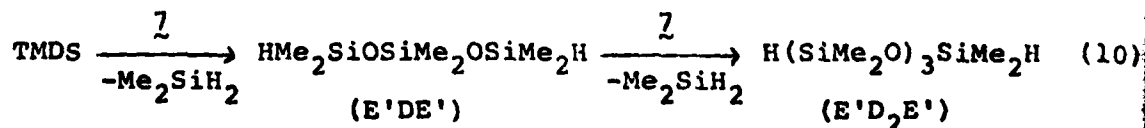
We immediately recognized that eq. 7 is a unique reaction in which a strong Si-O bond is cleaved in a neutral, non-aqueous solution at room temperature.¹⁴ The reaction (7) may be viewed as a metal-catalyzed exchange of R_3SiO -groups for H- on silicon (hereinafter denoted as a SiO/H exchange), viz. eq. 8 (the exchanging groups are underlined).



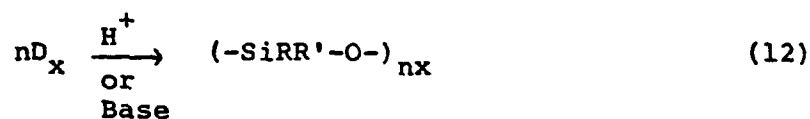
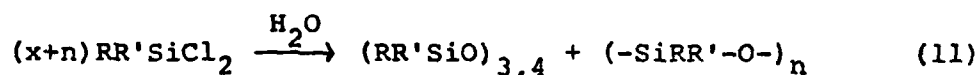
It was postulated that the strain inherent in the four-membered metallacycle weakened the Si-O bond and allowed its facile cleavage into coordinated silylene and silanone (eq. 9).^{13,14} Indeed, the crystal structure determination of complex 6 showed the Si-O-Si angle to be 99.8°, considerably smaller than the usual 130°-150° found in unstrained siloxanes.¹⁵ The large Si-O-Si angle in siloxanes has been attributed to the effects of (p-d) π bonding between oxygen and silicon. Therefore, a decrease in the Si-O-Si angle would imply loss of p_n-d_n bonding and consequent weakening of the Si-O bond. In fact, the Si-O bond length (1.68 Å) in 6 is somewhat longer than Si-O bonds in unstrained siloxanes (1.63-1.65 Å).



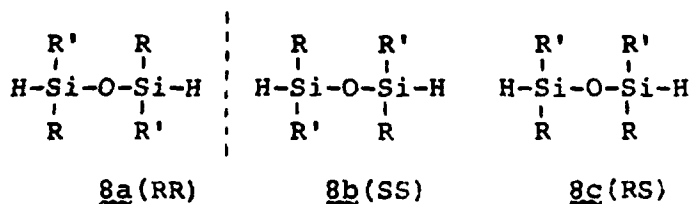
A complex mechanism was proposed whereby the complexed silanone (Me₂Si=O) in 7 was then inserted into the Si-H bond of the excess TMDS in solution. As the concentration of the trimer (E'DE') increased, the Me₂Si=O could then insert into its Si-H bond to give tetramer (E'D₂E'), and so on (eq. 10).



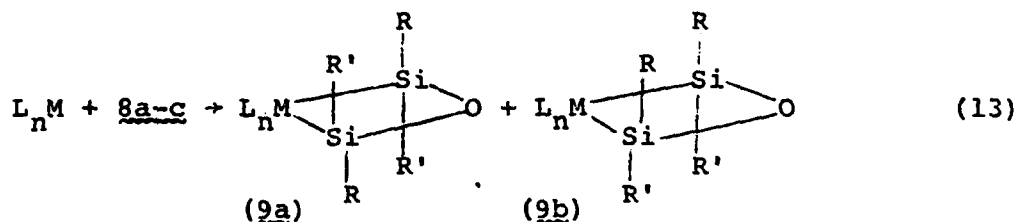
Reaction 7, the metal complex catalyzed oligomerization of disiloxanes, potentially represented a new route to polysiloxanes. The normal method of preparing polysiloxanes involves the hydrolysis of dialkyldichlorosilanes (eq. 11) to give linear polymer and cyclics (D_x , $x=3,4$). The cyclics may be polymerized in turn to linear polymer by acid or base catalysis (eq. 12). In these polymerizations, all the SiOSi bonds are redistributed and loss of any possible stereoregularity results.



The metal complex-catalyzed polymerization of disiloxanes of the type, $(HRR'Si)_2O$ (8), presents some intriguing possibilities. Disiloxane, 8, would normally be found as a mixture of three stereoisomers: a (*d,l*)-pair of enantiomers (8a,b) and the *meso*-diastereomer, 8c. These isomers are shown with the R,S nomenclature below. If the insertion of the metal into the Si-H bond proceeds with

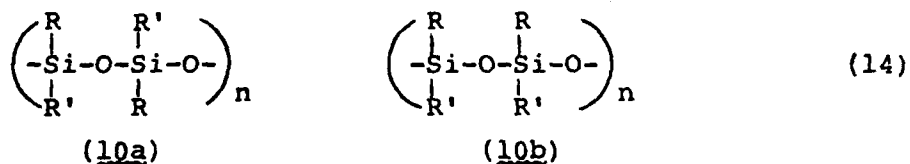


retention of configuration at silicon,¹⁶ then two types of metallacycle, 9a, b, would be formed from the mixture of three isomers, 8a-c, e.g. shown in eq. 13. The RR or SS



isomers would give only the transoid metallacycle, 9a, while the RS isomer would give only the cisoid structure, 9b.

We reasoned that if these metallacycles were indeed the catalytically active species in the oligomerization of the disiloxanes, 8a-c, then metallacycles 9a might lead stereoselectively to syndiotactic polymer, 10a, and the cis-metallacycle, 9b, to isotactic 10b. Furthermore, if metalla-



cycles 9a and 9b differ in energy by only ~3 kcal/mole as a result of 1,3-cross ring, steric interactions of the R,R' groups, then the lower energy isomer would be formed with a 100:1 preference over the higher energy isomer, leading ultimately to the selective polymerization of only one of the two forms 8a,b or 8c and giving essentially pure stereoregular silicone. It was with this objective in mind that

we started our investigations into the metal complex-catalyzed oligomerizations of disiloxanes.

EXPERIMENTAL METHODS

Analytical procedures. The oligomeric siloxane products were analyzed by GC and GC/MS methods. The analytical column employed was a 14' x 1/8" S.S. column packed with 5% SE-30 on Chromosorb WHP (80-100 mesh) with He as the carrier gas at a flow rate of 10 mL/min. Typical GC conditions were: injector, 250°C; detector, 300°C; temperature program, 2 min. at 40°C, then increase at 4°C/min. to 225°C. Mass spectra were recorded on a Finnigan 4000 quadrupole spectrometer interfaced to the temperature programmable GC column and controlled by the INCOS data acquisition system.

In those instances where MS alone could not differentiate the products, e.g. between isomers, the products in question were separated by preparative GC and analyzed by ^1H or ^{13}C NMR spectroscopy. Parent peaks were located by their mass chromatograms (mass vs. time) or by using chemical ionization. Once a compound's identity was definitely established, its spectrum was stored in a computer library, and all future occurrences of that compound in mixtures could be readily ascertained by comparing its mass spectrum to that in the library peak for peak.

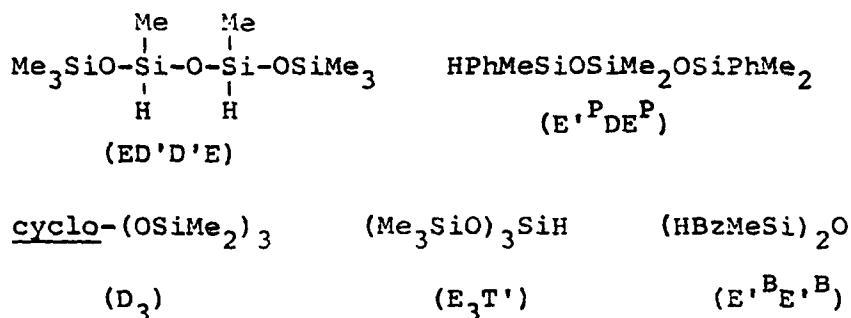
Redistribution Reactions. The conditions for each run are listed as footnotes in the Tables. A typical procedure is described here. Tetramethyldisiloxane (42 mmole) was added to 25 mL of a benzene solution containing 200 mg (0.26 mmole) of $L_2Ir(CO)Cl$ under a N_2 atmosphere. The reaction flask was equipped with a reflux condenser, N_2 inlet, and gases were vented through an oil bubbler attached to the top of the condenser. During the run, a static N_2 -blanket was maintained over the reactants. After heating in an oil bath for a given time, the solvent was stripped off under vacuum (ambient temperature) and the residue and solvent fractions analyzed as described above. During kinetic runs, the reaction flask was also fitted with a small, septum-tipped sidearm for periodic withdrawal of samples.

NOTATION

An abbreviated notation for siloxanes will be used where appropriate. The siloxane is denoted according to the functionality of the silicon and is based on the premise that the "normal" organic substituent is the methyl group. Thus, we use: E (end group) = $Me_3SiO_{1/2}^-$, D (difunctional) = $-O_{1/2}SiMe_2O_{1/2}^-$, T (trifunctional) = $MeSiO_{3/2}$, Q = $SiO_{4/2}$. A primed letter indicates H for Me substitution, i.e. $D' = HMeSiO_{2/2}$, $E' = HMe_2SiO_{1/2}^-$, etc., and a superscript "P" or "B" indicates Phenyl or Benzyl substitution for methyl, e.g. $E^P = PhMe_2SiO_{1/2}$. Two superscripts indicates

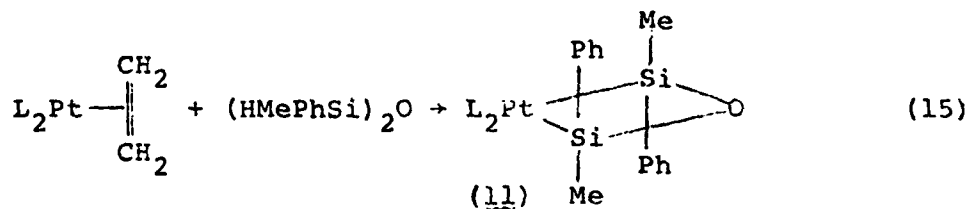
a double substitution for methyl, e.g. $E^P = HPhMeSiO_{1/2}$.

Some examples of the use of this notation are given below:



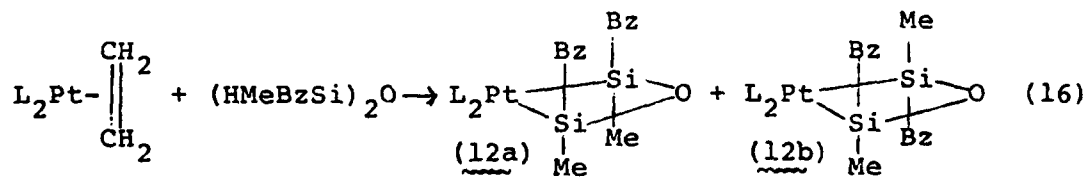
RESULTS AND DISCUSSION

Our initial premise that 1,3-cross ring interactions might lead to stereoselective formation of one isomeric metallacycle (e.g. 9a over 9b) from a mixture of stereoisomeric disiloxanes was quickly confirmed by the synthesis of the platinacycle, 11 (eq. 15, $L = \text{Ph}_3\text{P}$).¹⁷ The ^1H -NMR

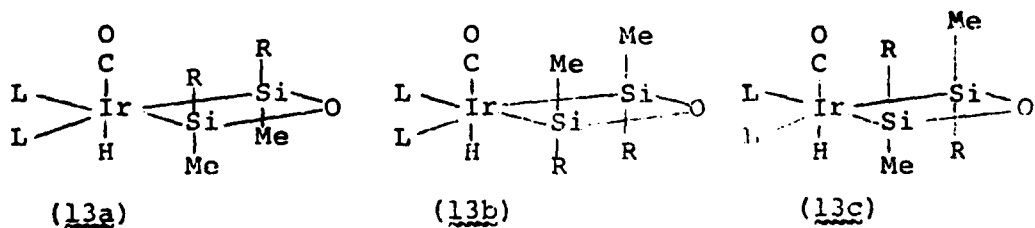


of 11 shows only one type of methyl group to be present, so the isolated material must be either all cis or all trans (11). The trans structure is favored on steric grounds.

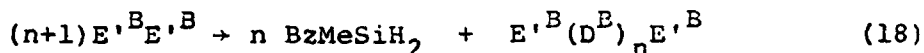
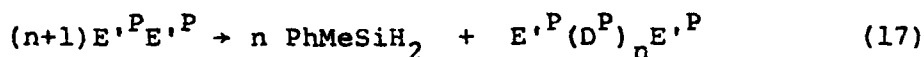
In contrast, reaction of the benzyl methyl disiloxane, $(\text{HMeBzSi})_2\text{O}$ ($\text{Bz} = \text{PhCH}_2-$), with $\text{L}_2\text{Pt}(\text{C}_2\text{H}_4)$ gave a mixture of the cis and trans metallacycles, 12a and 12b, in roughly equal amounts as judged from the NMR spectrum. Apparently, the benzyl group can swing around and lessen the 1,3 interactions to the point that the energy difference between 12a and 12b is minimal.



In a similar fashion, $(\text{HMeBzSi})_2\text{O}$ reacts with $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ to give a mixture of all three possible metallacycles, 13a-c ($\text{R} = \text{Bz}$).¹⁷ Lack of stereoselectivity is also observed when the octamethyltetrasiloxane, ED'D'E ($=[\text{H}(\text{Me}_2\text{SiO})(\text{Me})\text{Si-}]_2\text{O}$) is allowed to react with $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$. Again, the spectral properties are consistent with the solid being a mixture of the three metallacycles, 13a-c ($\text{R} = \text{Me}_3\text{SiO}$).¹⁸ The reaction of $(\text{HMePhSi})_2\text{O}$ with $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ is even more complex and the nature of the products is not definitely established.



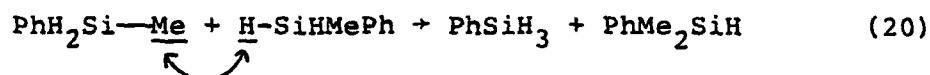
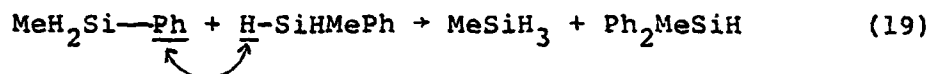
The metallacycle, 11, and several other metallacycle precursors were examined for their catalytic activity in the redistribution or oligomerization reactions of $(\text{HRMeSi})_2\text{O}$ ($\text{R}=\text{Ph}, \text{Bz}$). If these disiloxanes were to react in the same manner as TMDS (eq. 7), then the expected products would be as shown in eq. 17, 18. The actual products



observed for the reaction of $(\text{HPhMeSi})_2\text{O}$ ($\text{E}'^{\text{P}}\text{E}'^{\text{P}}$) are shown in col. 1 of Table I. Some monosilanes, e.g. Me_3SiH and PhMe_2SiH , are found, but none of the expected PhMeSiH_2 is present. However, some of the expected oligomeric products, e.g. $\text{E}'^{\text{P}}\text{D}_{1,2}^{\text{P}}\text{E}'^{\text{P}}$ (i.e. the lowest two members of the oligomers shown in eq. 17), are indeed present. In addition to these products, there is a variety of other products which appear to be the result of redistributing the methyl, phenyl, and hydrogen groups attached to silicon.

The formation of the monosilanes as indicated in Table I suggested that reaction 17 does occur, but the initially produced PhMeSiH_2 undergoes secondary rearrangement to give the final products shown. Accordingly, PhMeSiH_2 was subjected to metal-catalyzed redistribution conditions, and it was observed that a rapid redistribution of all the groups on silicon occurs to give the products shown in Table II. For example, eq. 19 and 20 detail the formation of Ph_2MeSiH

and PhMe_2SiH , emphasizing the nature of the exchanges (Ph for H and Me for H, or Ph/H and Me/H, respectively).



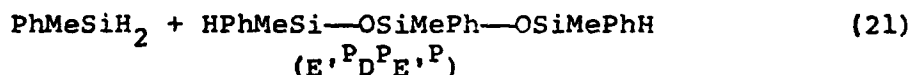
These rearrangements of Si-C bonds are probably close to being thermoneutral, so that the driving force is essentially entropic, especially when a volatile substance, e.g. MeSiH_3 , Me_2SiH_2 , etc., may be expelled from the reaction. In fact, recent results show that the rate at which volatiles are removed from the reaction can be rate limiting and also effects the distribution of products. For the case at hand, a mass balance for the products shown in column 2 of Table II reveals that the groups unaccounted for are in the ratio, 1Me:1Si:3H, i.e. MeSiH_3 is the principal volatile product.

Column 3 of Table II shows that the rhodium catalyzed disproportionation of PhMeSiH_2 is very similar to the iridium catalyzed reaction except that disilanes, e.g. $(\text{HMePhSi-})_2$, are also formed. This result is in accord with that of Ojima et al.¹⁹ The formation of disilanes seems to be a general result when rhodium or platinum based catalysts are used.

We have observed that the rate of metal catalyzed disproportionation of organosilanes is in the order,

$\text{RSiH}_3 > \text{R}_2\text{SiH}_2 \gg \text{R}_3\text{SiH} \gg \text{R}_4\text{Si}$. Trialkylsilanes, R_3SiH , disproportionate only very slowly under our conditions. The tetraalkylsilanes, R_4Si , are essentially inert under the mild conditions reported to date. Given this order of activity, monoalkylsilanes, e.g. PhSiH_3 , which are the expected products of certain exchange reactions (Cf. eq. 20), would undergo further, rapid exchanges and would not be observed.

Returning our attention to the products shown in Table I, the mono- and disilanes are ascribed to products from the redistribution of groups on PhMeSiH_2 produced by the reaction shown in eq. 17. The desired, oligomeric products, $\text{E}'^{\text{P}}_n\text{E}^{\text{P}}$, are formed in SiO/H exchanges as shown in eq. 21 for the first member of the series ($n=1$). The remaining

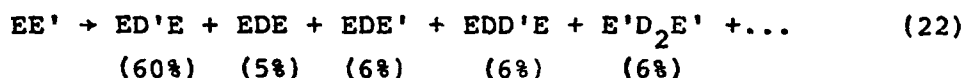


disiloxanes, e.g. $\text{E}'^{\text{P}}_1\text{E}^{\text{P}}$ ($= \text{HPhMeSiO}-\text{SiMe}_2\text{Ph}$), are formed as a result of Me/H , Ph/H , and Ph/Me exchanges on the starting disiloxane, $\text{E}'^{\text{P}}_1\text{E}^{\text{P}}$, and on the oligomeric siloxane products.

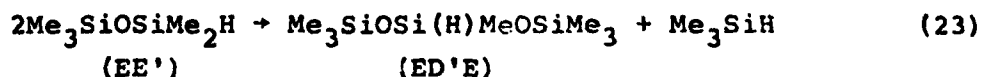
The benzylmethyl disiloxane, $\text{E}'^{\text{B}}_1\text{E}^{\text{B}}$, was also subjected to the redistribution reaction and results similar to those found for $\text{E}'^{\text{P}}_1\text{E}^{\text{P}}$ were observed. The lower boiling mono-silane fractions were composed of redistribution products of BzMeSiH_2 , e.g. BzMe_2SiH (36%), Bz_2MeSiH (30%), and

disilanes, e.g. (HBzMeSi-)₂ (11%) were found.

At this point, it appeared very likely that the "metallacycle" mechanism,¹³ if operative at all, was not the sole mechanism for redistributing the organic groups on siloxanes since the dialkylsilanes, R₂SiH₂, undergo a very rapid exchange. In order to further confirm this, several other substrates were subjected to redistribution catalysis. Pentamethyldisiloxane, Me₃SiOSiMe₂H(EE'), should be incapable of readily forming a four-membered metallacycle since the second silicon lacks a reactive Si-H functionality. However, this disiloxane does undergo a slow redistribution in the presence L₂Ir(CO)Cl (2 mole %) at 70°C to give predominately ED'E, as well as lesser amounts of other Si₃, and Si₄₋₇ polysiloxanes (eq. 22).¹⁸ A rather surprising facet of this



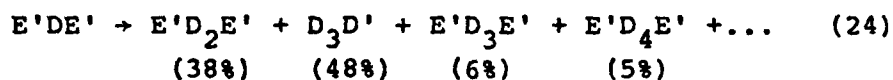
redistribution is that the ED'E is the result of a SiO/Me exchange (eq. 23) which is an unexpected result since Si-H bonds are much more reactive toward low-valent metal complexes than Si-C or Si-O bonds. Thus, a SiO/Me exchange is the result of compounding two "improbable" bond cleavages.



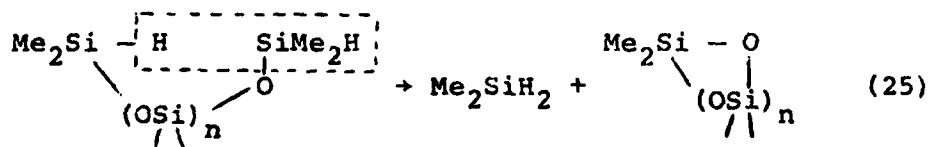
All of the redistribution reactions of disiloxanes initially exhibit a rapid, brief drop in disiloxane

concentration, followed by a slow zero-order rate of consumption. From the zero-order portion, a turn-over number of 1.1×10^{-3} moles $EE'/(mole\ Ir)/min.$ may be obtained. This is only 16 times slower than the observed turn-over number for TMS (E'E') under comparable conditions.¹⁸ This modest difference in rates again indicates that a special metallacycle mechanism is not the primary mechanism for the redistribution.

The trisiloxane, E'DE', also undergoes a slow redistribution in the presence of $L_2Ir(CO)Cl$ at $70^\circ C$ to give the products shown in eq. 24.¹⁸ The cyclic product, D_3D' , may



arise from the "internal" SiO/H exchange on E'DD'DE' (an expected product from E'D/Me exchange on E'DE') as shown in eq. 25.

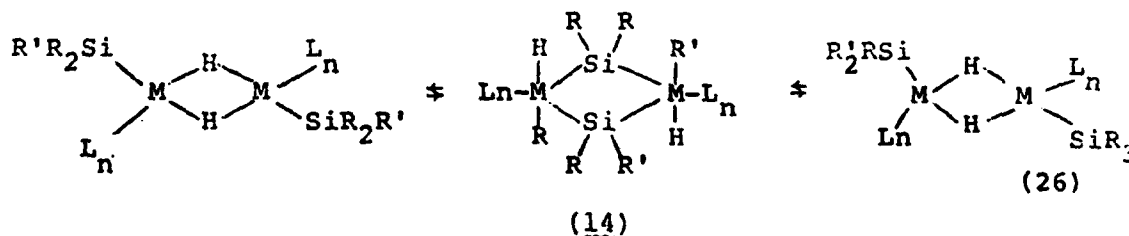


These results forced a re-examination of our working hypothesis. What kind of mechanism could be invoked to explain these results? Especially disturbing was the preponderance of SiO/Me exchanges which are difficult to rationalize on the basis of known silyl-transition metal chemistry.

Classifying the observed products according to their exchange type reveals that in the $L_2Ir(CO)Cl$ -catalyzed redistribution of TMDS (E'E'), 86% of the exchanges are SiO/H and 24% are SiO/Me. With L_3RhCl as catalyst, only 50% of the products come from SiO/H exchanges.

It is known that low-valent metal complexes rapidly insert into Si-H bonds, but will insert into Si-C or Si-O bonds only very slowly in most circumstances. (In fact, a preferential insertion into a Si-C or Si-O bond over Si-H has never been observed.) The mechanistic question then reduces to the question of how the Si-C and Si-O bonds are activated when attached to a silicon bearing an Si-H bond (keeping in mind that the rate of R_2SiH_2 exchanges is much faster than the rate of R_3SiH exchanges).

In order to account for the Si-C and Si-O bond activation, we proposed that dinuclear complexes, e.g. 14, are produced in the reaction mixture, and that these dinuclear complexes are responsible for the observed SiO/Me, R/R', etc. exchanges (eq. 26).²⁰



If dinuclear complexes are indeed the catalytically active species in the exchange reactions, then immobilizing

the metal centers on solid supports should inhibit SiO/Me exchanges, but possibly allow the SiO/H exchanges to proceed through mononuclear species. This hypothesis was tested by adsorbing the catalyst precursors on a variety of inorganic supports, e.g. alumina, silica, or alumina-silica. Indeed, the reactions of E'E' (eq. 7) proceeded much faster and gave higher selectivity for the desired SiO/H exchange (see Fig. 1). The most dramatic increase in selectivity occurred with 1% L_3RhCl on γ -alumina (followed by heating the catalyst to 70° for 4 hr. in vacuo). This catalyst gave a SiO/H exchange selectivity of 99%, compared to the 50% selectivity of L_3RhCl as a homogeneous catalyst. In no case was the desired selectivity less than about 93% at catalyst loadings of 1% or less. Higher catalyst loadings gave lower selectivities, a result consistent with dinuclear (adjacent) metal centers causing SiO/Me exchange, and mononuclear centers giving SiO/H exchange.²¹

SUMMARY

Certain transition metal complexes of Pt, Rh, and Ir have been found to be catalyst precursors for a redistribution reaction of siloxanes which leads to polysiloxanes. Analysis of the oligomeric products reveals that the predominant redistribution is one which exchanges groups α - to the Si-H functionality and that these groups exchange predominately with the Si-H group. High selectivity for

SiO/H exchange is achieved with complexes supported on inorganic oxides, e.g. SiO_2 , Al_2O_3 , etc.

Further work in progress includes the extension of the heterogeneously catalyzed reaction to disiloxanes of the type, $(\text{HRMeSi})_2\text{O}$ ($\text{R}=\text{Ph}$, $\text{CF}_3\text{CH}_2\text{CH}_2-$, etc.) with the aim of establishing the stereochemistry of the resulting oligomers. Should the reaction prove to be stereoselective, conditions will be sought which would lead to high molecular weight, stereoregular silicones. Such polymers may exhibit interesting properties, e.g. piezoelectricity. Concurrent work in progress has also shown that selective ring opening polymerization of cyclotrisiloxanes of the type, $(\text{RMeSiO})_3$, can give stereoregular polymers under the appropriate conditions. These results will be communicated in due course.

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Table I. Redistribution Products of 1,3-dimethyl-1,3-diphenyldisiloxane ($E^P E^P$).^a

<u>Product</u>	<u>Col. 1^{b,c} area %</u>	<u>Col. 2^{d,e} area %</u>	<u>Col. 3^{e,f} area %</u>
PhMe ₂ SiH	4.8	5.9	9.1
Ph ₂ MeSiH	12.2	24.5	75.5
Ph-Ph	0.1	6.5	2.7
MePh ₂ SiSiPhMeH	9.0	33 ^g	-
MePh ₂ SiSiPhMe ₂	5.4	0.6 ^h	-
$E^P E^P$	2.9	5.1	-
$E^P E^P$	10.3	3.6	-
$E^P E^P P$	6.0	0.3	-
$E^P D^P E^P$	7.2	-	-
$E^P D^P_2 E^P$	29.3	-	-

- a) Only those products which constitute ca. $\geq 5\%$ of the total are shown.
- b) 0.6 mole % 6 as catalyst in benzene at 60°C for 48 hr, 77% conversion.
- c) Area % of products only, starting material and solvent removed.
- d) 4.8 mole % Rh(acac)(C₂H₄) catalyst precursor, benzene solution, 40°C for 1 hr, ~20% conversion.
- e) The GC column for these runs was not heated high enough to elute the high boiling polysiloxanes.
- f) 0.5M $E^P E^P$, 1.8mm L₂Ir(CO)Cl in benzene at 40°C for 38 hr, ~60% conversion.
- g) Incomplete GC separation from HMePhSiOSiPhMeEt. The Et-group comes from the hydrosilation of the C₂H₄ in the catalyst precursor.
- h) Incomplete GC separation from a trace of EtMePhSiOSiPhMe₂.

Table II. Redistribution Products of PhMeSiH_2 .

<u>Products</u>	<u>Col. 1^a</u> <u>area %</u>	<u>Col. 2^b</u> <u>area %</u>	<u>Col. 3^c</u> <u>area %</u>
Me_2SiH_2	3.3	-	-
PhMeSiH_2	10.5	-	43.3
PhMe_2SiH	9.8	22.6	8.4
Ph_2SiH_2	14.0	-	0.6
Ph_2MeSiH	61.0	58.6	40.1
Ph_3SiH	1.4	18.8	1.2
$(\text{HMePhSi})_2$	-	-	6.4

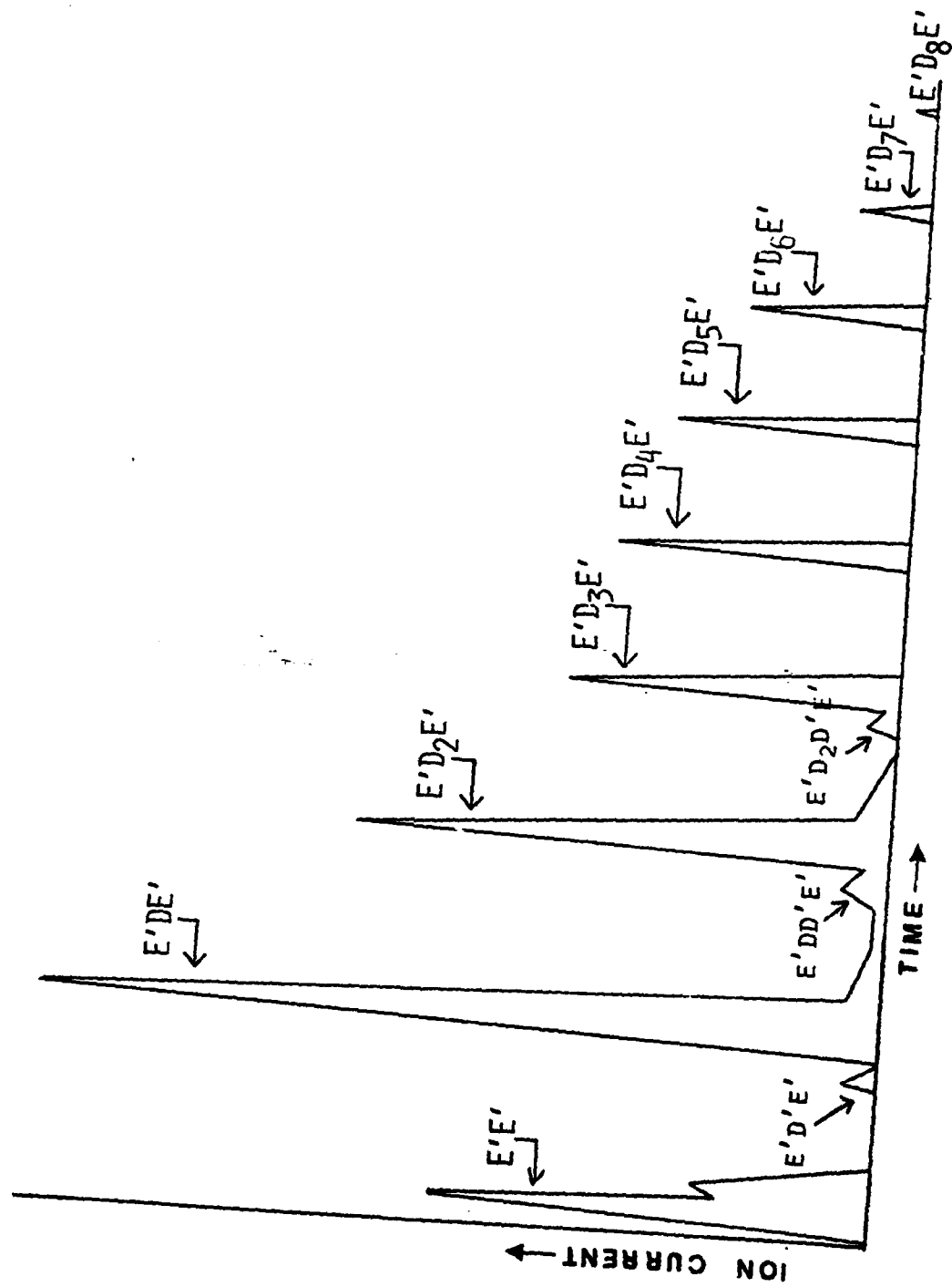
a) 5 mole % $\text{IrL}_2(\text{CO})\text{Cl}$ in benzene at 80° for 1 hr.

b) 5 mole % $\text{IrL}_2(\text{CO})\text{Cl}$ in benzene at 80° for 24 hr.

c) 4 mole % RhL_3Cl in benzene at 80° for 30 min.

Caption to the Figure

Figure 1. Total ion GC trace of the mixture resulting from the redistribution reaction of tetramethyldisiloxane (E'E'), catalyzed by 1% L_3RhCl ($L=Ph_3P$) on γ -alumina (calasied at 70°C for 4 hr in vacuo).



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